CHEMISTRY IN LASERS: QUANTUM STATES IN DYE LASERS

By

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In a dye laser the quantum states of the optically active molecules comprise a photon density dependent time-oriented sequence, requiring a two-dimensional *eigenvalue spectrum matrix*, rather than the usual one dimensional array used in spontaneous fluorescence. The mathematical representation of the time-oriented sequence of quantum states is a countable finite Markov chain, and a holomorphic map containing the eigenvalues includes both the tardyon and tachyon solutions, the tardyon-Hermitian matrix being a special case. Because different quantum states dominate the spontaneous and the laser emitter particles, altered chemical properties and reactions are predicted for an optical resonant cavity.

In a previous paper dealing with chemistry in lasers [1] the fluorescence excitation and emission spectrum of a molecule in solution showing a Stokes 0—0 loss[2] [2, 3] was compared to a 3-level and 4-level laser. The comparison revealed a close similarity between the fluorescence spectrum and a 4-level laser. Information on 3-level and 4-level lasers, including the advanteges of the latter, is available in standard texts [4, 5], and in the present paper the role and significance of an optical resonant cavity is limited to the alteration of the effective radiative lifetime of the

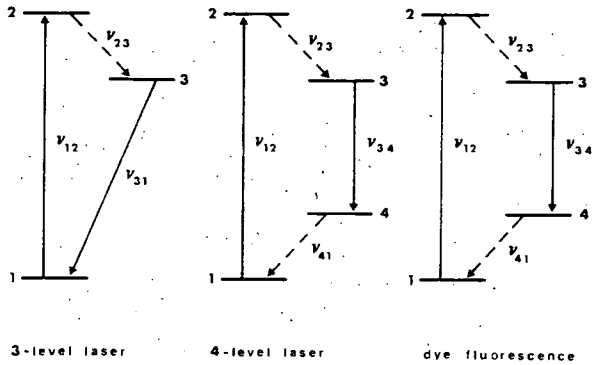

Fig. 1. Comparison of the energy levels of a fluorescor showing a Stokes 0—0 loss with 3-level and 4-level lasers (cf. text and references therein for details).

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[2] The separation of the 0—0 excitation and the 0—0 emission bands, where the vibrational energy levels are being identified by "0—0".

fluorescors; other consequences of laser action on chemistry [6] are discussed in a continuation paper [7].

To summarize the earlier conclusions [1], we note (Fig. 1) that in the system characterized by a Stokes 0—0 loss, absorption of a photon by a relaxed ground state molecule $({}^1R_0(l_1))$ results in a metastable electronically excited singlet $({}^1R^*(l_2))$ that will undergo a molecular relaxation to a state labelled ${}^1R^*_{fc}(l_3)$ (the Franck—Condon relaxed excited state). Emission of a photon having energy $E_{l_3}-E_{l_4}$ from ${}^1R^*_{fc}$ results in a metastable ground state molecule $({}^1R_0(l_4))$ that will undergo a molecular relaxation to ${}^1R_0(l_1)$. An attempt to represent this simple process in terms of two potential energy surfaces (one for the excited and one for the ground state), a representation that is very common in the literature [8] as having been derived from the 'Harmonic Oscillator' model in the manner found in standard texts on physical chemistry [9], is futile: the Stokes 0—0 loss cannot be represented by only two potential energy surfaces (cf. Fig. 2). An examination of the molecular relaxation taking place between levels 2 and 3, and 4 and 1, in Fig. 1, indicates that a series of quantum states must be dealt with. The changes in the solvent cage, on the one hand, result in a shift of the *zero-point energy* [9] of the potential energy surfaces of Fig. 2; on the other hand, the solute-solvent interaction and geometric changes of the dye molecule are closely related to a time-evolution process that affects the *molecular force constants* themselves. In effect, during the relaxation process that takes the molecule from level 2 to level 3, the quantum state appropriate to describe ${}^1R^*_{fc}$ cannot be used, instead, a representation appropriate to the time-evolving sequence of *precursor states* is required. There is no single quantum mechanical operator available to generate the entire time evolving sequence of precursor states in a useful manner[3], hence we have to consider some form of a discontinuous representation of the Stokes

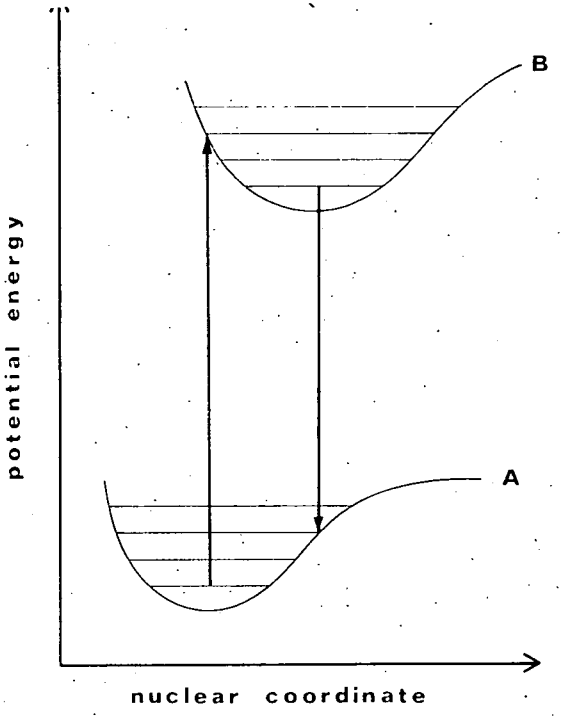

Fig. 2. Usual hypersurface representation of optical excitation and emission. It should be noted that a separation of the 0—0 excitation and 0—0 emission bands is not possible here, hence this model is unsuitable for compounds whose luminescence is characterized by a Stokes 0—0 loss.

[3] We consider the empty formalism of writing a time-dependent Schrödinger equation for large solvated dye molecules as less than useful.

0—0 loss, in the manner of Fig. 3. By taking the time-scale of the creation and annihilation of a photon as 'instantaneous', there are corresponding excited and ground states, between which dipole radiative processes occur (cf. levels i and j in the R_0 and R^* brackets in Fig. 3). For each pair of states such as $R_0(i)$ and $R^*(i)$ there exists an eigenvalue spectrum that can be considered as a one-dimensional matrix. Taking into account all the quantum states in the R_0 and R^* brackets, the full eigenvalue spectrum of the evolving sequence of states is a two-dimensional matrix. From a mathematical standpoint it is of great significance that the sequence of states is "time-oriented", for one may use a transition matrix function $P(t)$, $t>0$, in mapping a continuous time Markov process [10] based on a finite number N of states. To obtain a countable finite Markov chain [11], it is necessary to observe the process at unit intervals of time; regarding these elements as defining points in the holomorphic map R^{N^2}, where R^{N^2} has coordinates x_{ij} $(i, j=1, 2, \ldots, N)$, and letting X be the matrix (x_{ij}), if

$$f(z) = \sum_{n=0}^{\infty} f_n z^n$$

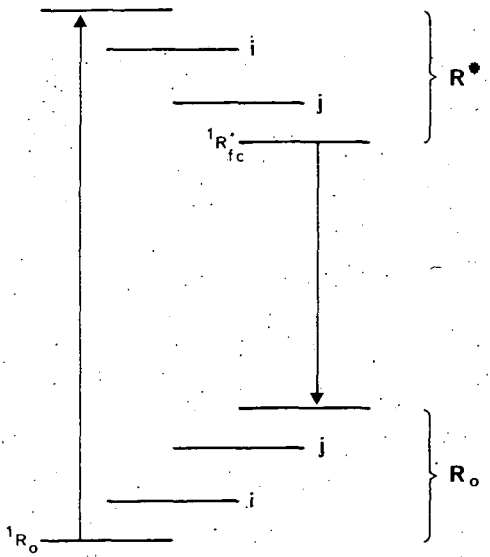

Fig. 3. Time-oriented sequence of potential energy hypersurfaces; emission of a photon results from transitions between excited and ground state manifolds having the same time coordinate (cf. levels i and j in figure for example).

is any power series with real coefficients and convergent for all z, we can define a differentiable map $F: R^{N^2} \to R^{N^2}$ by

$$F_{x_{ij}} = y_{ij},$$

where

$$y = fx = \sum_{n=0}^{\infty} f_n x^n;$$

then the Jacobian matrix of F has eigenvalues

$$\mu_{ij} = \frac{f(\lambda_i) - f(\lambda_j)}{\lambda_i - \lambda_j}$$

where λ_i are eigenvalues of X, and the expression is taken to be equal to $f'(\lambda)_i$. The *map* defined by $X \to exp\, X$ is locally homeomorphic except possibly when X has a pair of eigenvalues differing by a non-zero multiple of $2\pi i$[4].

As can be seen from the foregoing discussion and figures, to represent the

[4] As has been shown by Sudarshan [13—15] the existence of tachyons is well expected; by the exchange of a Hermitian matrix pertaining to tardyons to a Hermitian matrix pertaining to like tachyons, a difference of $-2\pi i$ vs. $2\pi i$ in the eigenvalues is predicted.

fluorescence of a compound showing a Stokes 0—0 loss in a rigorous manner, one must take into account a sequence of quantum states, and the mathematical representation involves a *countable finite Markov chain* [11]. What remains unanswered is a practical question: what is the error introduced in terms of "measurables" when the rigorous representation is forsaken in favour of the more simple one indicated by Fig. 2: In spontaneous fluorescence, if the fluorescence lifetime τ_f of R^* (τ_f defined by $I/I_0 = exp(-t/\tau_f)$ in the usual manner) is one nanosecond, then most of the excited molecules emitting photons will be characterized by R^*_{fc}, the Franck—Condon relaxed state. Accordingly, in case of spontaneous fluorescence the process may be represented, from a pragmatic standpoint, in terms of the simplified representation of Fig. 2. This empirically justifiable treatment has been adopted in the literature to treat quantum states in dye lasers also [12]. This extension is unjustifiable; it serves to illustrate how pragmatic considerations, in the absence of recourse to fundamental principles, can lead to erroneous conclusions.

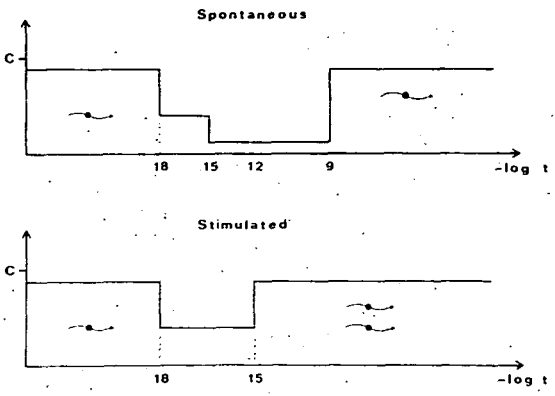

Fig. 4. A comparison of the time evolution of electronically excited states under spontaneous and stimulated emission conditions, revealing the predominance of 'early' time elements in the latter case. Ordinates represent the velocity of the highest velocity particle in the interaction sphere, abscissae represent time. This figure illustrates the extreme situation where, at a very high photon density, the stimulated emission process will occur before the excitation energy is substantially delocalized from the electric dipole vector of the molecule

As Fig. 4 indicates, under spontaneous emission conditions the simplified representation totally breaks down, for at high photon densities the lifetime of R^* will be quite different from τ_f, and the principal emitter will be a 'precursor' of the Franck—Condon relaxed state. Whenever different quantum states are required to describe an assembly of atoms or molecules, by definition it is expected that chemical and physical properties of the ensemble will also change. From this fundamental principle we may categorically state that chemistry in lasers is expected to yield results that do not coincide with the behavior of the same compounds under ordinary conditions. Detailed considerations and specific examples of chemical anomalies in a laser cavity will be discussed subsequently.

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ХИМИЯ ЛАЗЕРОВ: КВАНТОВЫЕ СОСТОЯНИЯ ЛАЗЕРОВ НА КРАСИТЕЛЯХ

Ч. П. Кестхели

Квантовые состояния оптически активных молекул лазеров на красителях представляют собой ориентированную во времени последовательность, зависящую от плотности фотонов, описание которых требует применения двухдимензионной матрицы спектра собственных значений, вместо обычно применяемых для описания спонтанной флюоресценции однодимензионной матрицы. Математическое представление ориентированных во времени квантовых состояний представляет собой исчисляемый конечный ряд Маркова и голоморфное изображение, содержащее собственные значения, в котором содержатся как тардионные, так и тахионные решения; тардионная матрица Гермита представляет собой особый случай. Вследствие того, что при спонтанной эмиссии и по лазерному механизму в частицах преобладают различные квантовые состояния, в оптическом резонаторе можно ожидать изменения химических свойств и реакций.